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NAVAL WEAPON COOK-OFF IMPROVEMENT CONCEPTS AND DEVELOPMENT

by

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for

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FOREWORD

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I. INTRODUCTION

Cook-off of ordnance due to accidental ship fuel fires has been a problem of escalating Navy interest ever since the two aircraft carrier disasters a decade ago. An extensive effort concentrates both on delaying an ordnance reaction long enough for fire fighters to quench the flames, and on reducing the severity of a reaction when and if it occurs.

The purpose of the report is to concisely inform the Aerothermochemistry Division at Naval Weapons Center (NAVWPNCEN), China Lake, of the major developments (along with accompanying stumbling blocks) directed towards a solution for cook-off; and in so doing, provide the Division with a flavor for the experimental techniques and analyses.

To initiate this task, the author first familiarized himself with the related field of ignition theory of solid propellants. Then, a thorough NAVWPNCEN library search was conducted, from which all confidential and unclassified reports published within the past 15 years that dealt with cookoff of solid propellant and explosive-loaded ordnance were studied. Additional information was obtained from Defense Technical Information Center and National Technical Information Service searches. Time did not allow for much information to be gathered from informal discussions or relevant unpublished material. Therefore, this presentation can only attempt to be as current and complete as NAVWPNCEN's technical library. (It should be noted that only <u>unclassified</u> material went into preparing this report).

In the body of this paper (Part II), sections are presented in order of increased complexity of concept and computer modeling solvability. In Section A, the early stages of a computer model that simulates cook-off conditions are discussed. In this one-dimensional model, all components, except the explosive, are considered inert. The unit has its "reaction" when the self-generated chemical energy gains cannot dissipate via conduction at some spot in the explosive. Although the model predicts cook-off times, it tells nothing about the extent of the reaction.

Chemically reactive insulative external coatings used to delay reaction times are discussed in Section B. Adaptibility to a model similar to that in Section A has already been accomplished. Application techniques that will eliminate direct heat paths plus methods that correct the resulting char's erosive and splitting properties are being investigated.

There are two obvious faults to the model in Section A. In actual ordnance items, there are generally more than one type of explosive charge, each having different autoignition (chemical runaway) temperatures. Also, it is evident from any ordnance component drawing that this is a three-dimensional problem--not a one dimensional one. One can therefore conclude that there are critical heat paths, weak links that transfer heat to locations that experience chemical runaway far before other areas would. Experimentally (Section C) these direct lines are discovered and eliminated. Retrofitting concepts are theorized and tested in Section D. In Section E, densensitizers, which when released from its liner matrix react to reduce the autocatalytic nature of an energetic material, are investigated.

Sections B through E appear to be adaptable to computer modeling. To unify these concepts with liner pyrolysis theory (Section F), one would need to include: (1) liner gasification rates, (2) thermoelastic properties of case, liner, and explosive, and (3) ignition theory for propellant cracks.

Those test methods, important yet not essential to the body of this report, are discussed in Appendix A.

II. LITERATURE SURVEY

A. Simplified Model

A one-dimensional transient temperature mathematical model was developed[1] that would predict reacting times to cook-off of an explosively loaded ordnance item immersed in a JP-5 fuel fire. The model operates with an explicit finite-difference approach on a multi-layered flat-plate analog of the item. Stability criteria for the differential equations has been determined. Each explosive system must be made geometrically compatible before using the model. Cook-off time is defined by the onset of a steep temperature increase usually occurring at the layer of the energetic material closest to the fire.

The energy equation balances the zeroth order Arrhenius chemical decomposition term with conductive and stored energy terms. At the unit's flame boundary, convective and radiative terms (absorption and emission) are balanced by a solid conduction term.

Tests were run that simulated reactions in Mk 81 and Mk 32 cylindrically shaped bombs. The bombs had three components. Radially outward, they were the explosive (H-6), an inert asphaltic hot-melt liner, and a steel case.

Allowances for flame build-up and extinction period were made. Quantification of heat transfer parameters such as flame temperature, heat transfer coefficient and radiant heat flux, had been discussed in previous papers.

Five different sets of thermal stability input parameters were used. Three pairs of activation energy and frequency factor (two from the 2 differential thermal analysis exotherms and one from the sole differential scanning calorimetry (DSC) exotherm) were combined with a chemical heat release term associated with either H-6's initial heat of reaction, H-6's heat of explosion, or a weighted sum of the heats of explosion of the H-6 components.

To verify the model, input was taken from previous fast cook-off test conditions. Computer and experimental times to reaction compared favorably. Subsequent computer runs were conducted in which flame temperature, hot-melt thickness, liner thermal conductivity, etc. were varied. A perturbation study was also made to determine reaction time sensitivity to input parameter error. (At the time this report was written, program adaptability to insulative coatings was being planned.)

B. External Coatings

Insulative coatings can either be (1) inert, (2) normally ablative (they form a char with very low thermal conductivity), (3) intumescent (they swell reducing conductive and convective heat transfer from the flame), or (4) some combination of the above three.

The Naval Air Test and Development Center[2] conducted a series of tests designed to evaluate different external coatings. Samples with steel backings were put into a JP-5 fuel fire of 10 Btu ft^{2}-s heat flux. The number of seconds per mil of sample required for the steel insulative interface temperature to reach either 500°F or 1000°F was recorded as the coating's thermal efficiency. These results were then fed into the Naval Surface Weapons Center (NSWC)/Dahlgren "TRUMP" Computer program and applied to the Mk 36 missile motor. Computer results indicated that only two external coatings (bearing what was considered to be the maximum tolerable thickness conducive to marginal effects on missile performance) would provide adequate insulation to prevent cook-off for at least 5 minutes. They were sheet material intumescents; AVCO and Pfizer Firex.

Fast cook-off tests supported these preliminary findings. Unfortunately, AVCO tended to split and provide a critical heat path to the propellant. This could be remedied (1) by applying an open weave glass cloth to support the char or (2) by providing alternating layers of non-intumescent material and AVCO. Firex, whose computer performance was not as good as AVCO, is competitive because it is less expensive.

In general, coatings can now be sprayed on to eliminate the direct heat paths at the sheeting material seams. Spraying is now an acceptable technique because its resulting non-uniformities in thickness have lately been found to be within missile performance specifications.

C. Critical Heat Paths

Fast cook-off tests were performed on the Sidewinder Missile System.[3] To isolate the ordnance's vulnerabilities, the experimental tests were conducted using both live and inert sections. Temperature-time curves were used to discover the critical heat paths. In this study, the most sensitive paths were (1) heat transfer through the motor case to the propellant as indicated by propellant/liner interface temperature rises averaging 5°F/s, (2) heat transfer to the warhead's fore end case/explosive interface, and (3) heat transfer to the igniter squib evidenced by an early acceleratory temperature climb due to comparably low autoignition (chemical runaway) temperature of this part. Recommendations included (1) using external coatings for the warhead and motor, (2) remachining the warhead charge further away from its case, and (3) using a phenolic interrupter to block heat passage to the squib.

D. Retrofitting

Five concepts for retrofitting Agile and Sidewinder Missiles[4] were experimentally tested by fast cook-off tests. Baseline demonstration motors had standard propellant and liner inside a steel tubing 6-inch O.D. and 24-inch length. The concepts tested were:

(1) Application of a conductive coating, such as copper, to achieve a leveling in heating effect.

(2) Application of an intumescent paint as sheet stocks.

(3) Multiple alternate layers of insulating material (polycarbonate film) and reflective material (aluminum foil).

(4) Grooving (machining into case) and slotting (removal of strips of coating) to create a weak point for early case rupture to effect a less severe, unconfined reaction.

(5) Reinforcement of the grooves in concept No. 4 with filler and surface coatings to delay reactions.

Thermocouples were placed at selected locations to record heat paths and discover the unit's weak links. For instance, liner melting was recorded (as an endotherm) at the liner case interface near a groove (concept No. 4). That the liner had liquified was apparent by the increased thermal conductivity noted by an ensuing rapid temperature rise at a thermocouple located radially inward from the groove at the propellant/liner interface. Seconds later there was an infinite temperature rise at the propellant's surface which was interpreted as a developing hole inward to the bore and ignition.

It should be noted from the results that even though insulation tends to delay reactions, the extent of reaction may be worsened because more heat is absorbed at the lower heat rates.

E. Desensitizers

H-6, a TNT- and RDX-based explosive, is triggered to an explosion by its first exotherm. According to DSC scans (40°C/min and 2 mg of sample), the exothermic maximum for the H-6 explosive is 500°F. One would wish to increase this temperature (i.e. delay reaction), but more importantly, reduce the magnitude of heat released by this exotherm. This could be accomplished by selecting an appropriate liner matrix (either silicone rubber-based, silicone resin-based, asphaltic hot melt, plastisol, or modern hot melt) and embedded desensitizer.[5]

In general, liners should have good thermoviscoelastic properties (see Section F) and be compatible with other ordnance material. Ideally, liner properties for these explosives (1) should not melt below 350°F to prevent explosive/case contact and early reactions, (2) absorb heat (by melting) between 350°-400°F, (3) release a desensitizer between 400°-500°F which serves to suppress the explosive's exothermic reaction (called an "endothermic effect").

Preliminary DSC tests were made with various desensitizers directly embedded in the H-6. Since mixing of this nature dilutes the explosive, additional tests were run with liner matrices (with desensitizers in them) and H-6. These tests were run to ensure that the desensitizer was released from the matrix and effectively interacted with the explosive. Small-scale fast cook-off tests, using approximately 3 pounds explosive, were then run in a pipe bomb (a cylindrical pipe with threaded caps). Material selection was based on the previous tests. A plastisol (35% s-trithiane-65% Denflex) yielded the longest cook-off time of 9 minutes.

F. Liner Pyrolysis

Vetter[6] proposed a failure mechanism hypothesis for rocket motors during fast cook-offs that was experimentally supported. Initially, as the ordnance is heated, the steel casing expands, creating tension at the liner/case interface. Separation results, followed by volume and pressure increases, as pyrolized liner gases are emitted. The temperature of the case in this localized region rises due to the decreased thermal conductivity of the gas. One of two events can now occur: these gases will weaken the bondline and pass through or around to the bore, causing a violent confined reaction; or the case will rupture, causing a less violent, unconfined reaction.

Temperature and pressure measurements recorded pyrolized gas paths and pressure buildups plus ignition points and burn spreads. Recommendations included (1) that there be further analysis of the thermoviscoelastic properties of both liner and propellant, (2) that liner be selected so an early clean separation be made from the case (this can be accomplished with polyether polyurethane), (3) that the case be designed so that it will vent at low pressures.

Fast cook-off tests were made on Shrike and Sparrow Missiles.[7] Again, in order to isolate vulnerabilities, tests using both live and inert sections with this systems warhead-fuse-motor-igniter-guidance control components were run. Additional data recorded were the times to reach the first exotherms at the liner case interface of the motor and the cavity paint/case or potting material/case interface of the warhead.

The scenario, supported by experimental results, was: exothermic liner pyrolysis leading to cracks in propellant (or explosive) due to pressurization with subsequent crack burning and pressure buildup followed by explosion.

Recommendations included (1) use of insulative coatings for warhead and motor, (2) incorporation of machine weakened warhead and motor bottoms, (3) surface modifications of propellant to reduce cracking under stress and (4) a means to inhibit the oxidizing agents in the pyrolized gases of cavity paints and potting materials.

In the preceding analysis, the author emphasizes that the heat released in the early exotherm triggers a lower autoignition temperature (as recorded at the energetic/insulator interface) than would occur without a "reactive" insulator. This seems exaggerated and unjustified.

To compare relative gasification activity of various rocket motor liners, Langerman[8] performed the following experiment: 3-inch diameter by 1/10-inch thick samples of six different types of liner materials were applied to steel plates made of rocket motor casing material. This was then hermetically enclosed with a glass window to allow for visual observation. The space between liner and glass was filled initially with one atmosphere nitrogen. Heat was provided by a propane bunsen burner whose maximum flame of 2000°F and heat flux of 13-16 Btu/ft^2-s was said to simulate worst-case full-scale fast cook-off conditions. Thermocouples recorded temperature at both steel/liner interface and the top of the liner. Pressure was recorded in the space above the liner. Heat flow was stopped when the pressure reached 100 psig; but, the run continued until the reaction was completed. The reactions of the six liners ranged from slight outgassings to violent pyrolysis.

III. RECOMMENDATIONS

It is suggested that a unified model incorporating all the concepts discussed in the body of this report be formulated and computerized. Besides predicting reaction times, the model should be able to discover the controlling critical paths. It is felt that the development and inclusion of the theory of propellant cracks[9] might make it possible to predict reaction severity. This model should also be made adaptable to a variably located fire in relation to the ordnance item.[10]

APPENDIX A

Determination of the energetic material's activation energy and frequency factor (Section A) is important because these two parameters appear in the Arrhenius term of the heat equation for cook-off. Compatibility tests (Section B) serve to inform the scientist as to the extent one component interferes with the independent predictable and desirable behavior of another. Slow cook-off times (Section C) provide information on the thermal stability of an explosive for both long-term storage and sterilization operations. Full-scale fast cook-off tests which simulate the actual fuel fire's effect on ordnance, and their preliminary cost-saving small-scale cook-off bomb tests are discussed in Section D.

A. Tests for Activation Energy (E) and Frequency Factor (A)

Joyner[11] performed isothermal decomposition experiments on energetic material of less than a gram at temperatures in which major decompositions were completed within tens of seconds to several days. Material was maintained in a partial vacuum to keep unconfined gaseous products closer to the explosive's surface. Acceleratory rate segments of the reaction curves (i.e. decomposed weight fraction versus time) were interpreted as zeroth order reactions, whereas deceleratory segments were regarded as first order reactions. Arrhenius plots (log reaction rate constant versus temperature inverse) were in general linear, indicating a simple reactive mechanism. From Arrhenius plots, E and A can be readily obtained for the temperature range and reaction of interest. As an additional note, log half-life versus temperature inverse curves will also be linear, since the reaction rate constant is inversely proportional to time for similar quantities of decomposition.

Pakulak and others[12-16] conducted the following series of tests:

Differential Thermal Analysis/Thermal Gravimetric Analysis (DTA/TGA) tests of 10-50 mg specimens record chemical reactions (exotherms and endotherms) by comparing the specimen's temperature change with that of an inert material. A typical heat rate is 3°C/min. Activation energies and frequency factors are determined from zeroth and first order Arrhenius plots obtained from weight loss data.

Differential scanning calorimetry tests also record chemical reactions by comparing energy inputs of the specimen with that of an inert substance. Heat rates are somewhat higher; 10 to 40°C/min. E and A are found from an equation by Kissinger that compares the peak temperature of reaction with heat rate.

Parr bombs handle a larger quantity of specimen (approximately one gram). The sample is put into an inert environment of Argon initially at 1 atmosphere pressure. Pressure changes measure weight loss from which A and E can be found for either first or zeroth order reactions.

Slow cook-off tests are isothermal experiments that involve one to five pounds of specimen. Samples, wrapped in aluminum foil, are put into electrically heated cylinders whose ends have pillows to allow for the quick release of cook-off gases. An "adiabatic approach" can be used to find E and A by plotting the log rate of change of the samples' center temperature at the instant after chemical runaway with the inverse of oven temperature. At this instant, it is assumed that all chemical energy released becomes stored energy and conductive losses are negligible.

B. Tests for Compatibility

The experiments of Joyner, mentioned in Section A, either consisted of pure specimens of explosive or samples of explosive compositely mixed with protective liner or additive material. Evidence of pressure spikes that followed rapid gasification, anomalies in reaction curves, and nonlinear Arrhenius plots indicative of a complex reactive mechanism, were signs of incompatibility between the materials. Most liner or additive materials merely catalytically increased the reaction curve steepness. These reduced half-lives are interpreted as somewhat faster cook-off times.

Pakulak used DTA/TGA scans to determine the compatibility of a protective liner with various gas-forming salts that were to be added to prematurely rupture the case in the event of a fuel fire. Any appreciable changes in each substance's individual decompositon rates, reaction temperatures, patterns, etc., when viewed compositely would indicate incompatibility. Most of the composites' scans were practically superpositions of the individual liner and salt scans; thus ensuring compatibility.

C. 500 Day Slow Cook-Off Test

Consider the instant just before chemical runaway in a slow cook-off process. At this instant, the object is essentially steady-state; all chemical energy is dissipated by conduction. Pakulak combines his experimental slow cook-off times with an empirical function derived by Zinn and Rogers, using this "steady-state approach" to predict a maximum safe oven temperature for no cook-off in a 500-day period. The Navy requires a minimum oven temperature of 85°C. (Extrapolations to large times appear unjustified in that the empirical function was derived from zeroth order kinetics, whereas the low oven temperatures necessary for 500-day cook-off imply first order kinetics.)

D. Fast Cook-off Tests

Small cook-off bombs serve as preliminary test. A sufficient quantity of explosive (2 pounds) to provide a thermal gradient for skin burn-off, is placed in a sealed oven and heated at approximately 2°C/s. Skin temperatures and pressures versus time are recorded, as are time and extent of reaction. To pass the test, no reaction larger than the mildest explosion is tolerated.

Full-scale fast cook-off tests are conducted at NAVWPNCEN's skytop and CT-4 sites and at NSWC, Dahlgren. Ordnance (with some live and other inert sections) is mounted on an A-frame, centered 3 feet above a fuel pit filled with JP-5 fuel. The flames are initiated by electric matches wrapped in gasoline soaked rags. Gasoline is also spread over the fuel's surface. Average flame temperatures should be approximately 1600°F for at least 15 minutes after flame build-up, and 1000°F flame temperature should be reached within the first 30 seconds. The extent of reaction is recorded as either detonation (severest), partial detonation, explosion, deflagration, or burning (mildest). The Navy requires no more than a burn during the first 5 minutes; and, no more than a deflagration beyond that point.

Propane, a cleaner fuel, is on occasion substituted for the JP-5 that is in a ship fuel fire. JP-5 furnishes smoke and propane doesn't. Smoke increases the radiative heat flux and also blackens an object to increase the absorptivity. Therefore, propane must burn in a temperature range of 2200-2300°F to put the same heat flux into the ordnance items as JP-5 burning in the 1500-1600°F range.

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